Hemin Functionalized Hybrid Aerogel-Enabled Electrochemical Chip for Real-time Analysis of H_2O_2

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S1 Experimental Section

1.1 Reagents and apparatus

Graphene oxide (GO) was purchased from XFNANO Materials Technology Co., Ltd. (Nanjing, China). MXene was acquired from Xiyan New Material Technology Co., Ltd. (Shandong, China). Hydrogen peroxide (H_2O_2) was obtained from Chuandong Chemical Co., Ltd., (Chongqing, China). Glucose (Glu), L-cysteine (L-cys), Dopamine (DA), and Ascorbic acid (AA) were acquired from Sigma-Aldrich

(Shanghai, China). Hemin, Potassium chloride (KCl), Sodium chloride (NaCl), L-lysine (L-lys), Asparagine (Asp), and Glycine (Gly) were purchased from Aladdin Biochemical Technology Co., Ltd (Shanghai, China).

The morphology was characterized by Field-emission scanning electron microscopy (FESEM, JEOL-6300F). The chemical compositions were examined by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi). Electrochemical tests including cyclic voltammetry (CV) and chronoamperometry (i-t) were performed on a CHI 660E electrochemical workstation (Shanghai CH Instrument, China). Electrochemical test was performed in 0.01 M phosphate buffer solution (PBS, pH 7.2).

First-principle calculations based on density functional theory (DFT) were performed using the DMol3 package in Materials Studio. The generalized gradient approximation (GGA) functioned with Perdew-Burke-Ernzerhof (PBE) was used to perform the unrestricted spin-polarized DFT calculations[1]. The Grimme (DFT-D3) was used to deal with the van der Waals interactions[2]. The convergence criteria for structure optimization and energy calculation were set to (a) an SCF tolerance of 1×10^{-6} hartree, (b) an energy tolerance of 1×10^{-5} hartree, (c) a maximum force tolerance of 2×10^{-3} hartree/Å, and (d) a maximum displacement tolerance of 5×10^{-3} Å.

1.2 Fabrication of hybrid aerogel

The hybrid aerogel (He@GMA) was synthesized through one-step hydro-thermal treatment and freeze-drying (Fig. S1a). Typically, 1 mL of Ti_3C_2 MXene colloidal suspension (2 mg mL^{-1}) and 4 mL of GO suspension (2.5 mg mL^{-1}) were fully mixed by ultrasound. Then, 5 mg of hemin was added and continued to sonicate for 15min. After that, 500 μL of L-Cys (50 mg mL^{-1}) was added and the mixture was treated at 90 ℃ for 6 h to form hemin incorporated hydrogel. The obtained hydrogel was thoroughly immersed in deionized water, followed by freeze-dried for 24 h to form He@GMA.

1.3 Construction of microfluidic electrochemical chip

5 μL of He@GMA dispersion (5 mg mL^{-1}) was first added on screen printed carbon electrode (SPCE) and dried at room temperature to form the sensing interface. The developed sensor was then integrated with a microfluidic chip, which consist of two components. One component (a) contains a groove that measures 38 (L) × 13 (W) × 0.5 (H) mm^3 (L=length, W=width, H=height) to perfectly fit the SPCE (Fig. S1b).

Another (b) contains a fluid channel that are measured with 1 (W) × 0.48 (H) mm^2 (Fig. S1c). Polymethyl methacrylate (PMMA) is used as the chip material and processed by numerical control machine tools. They are assembled by adhesive ester.

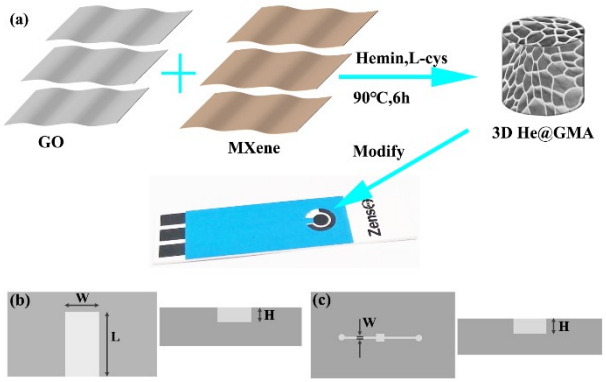

Fig. S1 Schematic diagram of the (a) 3D He@GMA fabrication process and (b,c) chip component.

S2. CV curves recorded in 5 mM $[Fe(CN)_6]^{3-/4-}$

Figure S2 shows the CV curves of different electrodes obtained in 0.1 M KCl containing 5 mM $[Fe(CN)_6]^{3-/4-}$. As observed, bare SPCE presents a pair of redox signals, which is enhanced after graphene aerogel (GA) modification, revealing a good conductivity of GA. Besides, reduced graphene oxide/titanium carbide MXene hybrid aerogel (GMA) modified SPCE shows a significantly enhanced signal. The reason may be that titanium carbide MXene with excellent conductive property could obviously promote the electron transfer. Further, hemin functionalized GMA shows the best electrochemical performance. The electroactive surface area of different modified electrodes was calculated on the basis of the Randled-Sevcik equation:

$$Ip = 2.69\times10^5 \times n^{\frac{3}{2}} A D^{\frac{1}{2}} \nu^{\frac{1}{2}} C$$

Where I_p is the peak current (A); n is the number of transition electrons of $[Fe(CN)_6]^{3-/4-}$(n=1); A refers to the effective surface area of electrode (cm^2); D means the diffusion coefficient, which is (6.7±0.02) × 10^{-6} cm^2 s^{-1}; ν means the scan rate (V s^{-1}); and C is the concentration of the redox reactant (5×10^{-6} mol cm^{-3}). The effective surface area of different modified electrodes was calculated in the tendency of GA/SPCE (0.112 cm^2) < GMA/SPCE (0.134 cm^2) < He@GMA/SPCE (0.158 cm^2), indicating that He@GMA owns the largest electroactive surface area.

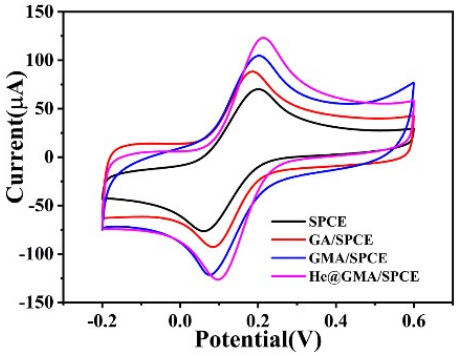

Fig. S2 CV curves recorded in 5 mM $[Fe(CN)_6]^{3-/4-}$.

S3. Plot of reduction current versus scan rate in PBS containing 2 mM H_2O_2

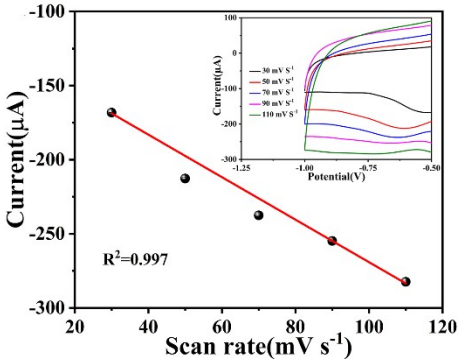

Fig. S3 Plot of reduction current versus scan rate in PBS containing 2 mM H_2O_2. Inset is the enlarged CV curves obtained at different scan rates.

S4. Current responses of the chip towards 200 μM H_2O_2 and 1 mM interferents

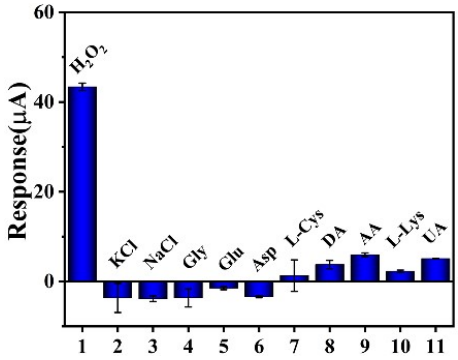

Fig. S4 Current responses of the chip towards 200 μM H_2O_2 and 1 mM interferents (n=3).

S5. Table S1 List of some reported electrochemical sensors for H_2O_2 Sensing.

Sensing materials	linearity range (μM)	LOD (μM)	Detection model	Ref.
MoS_2/CC	5-235/435-3000	1.0	CE	3
[Mo-oxo]n	0.05-5000	0.23	GCE	4
Pt-Cu_2O	10-6000	10.3	GCE	5
Cu-Ru/LIG	10-4320	1.8	GE	6
He@GMA	1-200	0.96	Chip	This work

CE: Carbon cloth electrode; GCE: Glass carbon electrode; GE: Graphene electrode

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